Growth of lower stratospheric HCl/Cly since 1993: observations from aircraft (ALIAS), balloon (MarkIV, FIRS-2), Space Shuttle (ATMOS), and satellite (HALOE) measurements

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Abstract. Measurements of HCl in the lower stratosphere (15-21 km) from aircraft, balloon, Space Shuttle, and satellite reveal a growth in its mean abundance relative to that of total inorganic chlorine (Cl_y) from $HCl/Cl_y = 57(\pm 5)\%$ in early 1993 to $75(\pm 7)\%$ by the end of 1997. This large growth of $31(\pm 9)\%$ in five years is ~6 times greater than model predictions that include heterogeneous chemistry on the diminishing volcanic aerosol from Mt. Pinatubo. This result, seen in HCl data sets of ALIAS (ER-2), MarkIV (balloon), FIRS-2 (balloon), ATMOS (Space Shuttle), and HALOE (UARS), is not understood.

Introduction

Seven years have passed since the massive enhancement in aerosol loading of the lower stratosphere following the June 1991 eruption of Mt. Pinatubo [*McCormick et al.*, 1995; *Jonsson et al.*, 1996], and the atmosphere has now returned to pre-eruption levels. Several studies [*Fahey et al.*, 1993; *Koike et al.*, 1994; *Webster et al.*, 1994a; *Sen et al.*, 1998] have compared measurements of NO_x with those of NO_y to conclude that the heterogeneous chemistry driving the large reductions observed in concentrations of stratospheric NO_x is well-understood. Reconciling observations of chlorine compound concentrations of the lower stratosphere to these same model calculations has, however, proved more problematic.

Despite the large impact on NO_x and ClO_x, photochemical model calculations incorporating the heterogeneous hydrolysis of N_2O_5 and $ClONO_2$ predicted only small changes in HCl amounts [*Salawitch et al.*, 1994; *Hanson et al.*, 1994], and little change in the HCl/Cl_y fraction with time [*Dessler et al.*, 1997]. *In situ* measurements of

HCl/Cl_y by JPL's Aircraft Laser Infrared Absorption Spectrometer (ALIAS) instrument [*Webster et al.,* 1993] in 1991/2 first challenged the notion that values significantly below the 80% of model predictions could occur. A recent study of the ALIAS data set from 1991-96 [*Webster et al.,* 1998] incorporated faster heterogeneous chemistry to show that air parcels with high aerosol loading exposed to temperatures below 205 K can experience enough chlorine activation to drive the HCl/Cl_y fraction below 50%.

However, model calculations that produce low HCl/Cl_y also produce relatively high ClO/Cl_y, in disagreement with simultaneous aircraft observations of HCl and ClO. In the SPADE ER-2 aircraft campaign of 1993, for example, in the absence of *in situ* measurements of $ClONO_2$, simultaneous measurements of ClO, NO, and O_3 were used to infer $ClONO_2$ abundances [*Stimpfle et al.*, 1994]. With an inferred fraction of $ClONO_2/Cl_y$ =14% (ranging from 6 to 28%), the measured ClO amounts implied that if Cl_y comprised mainly HCl and $ClONO_2$, then HCl/Cl_y should be ~86%, compared to the values of 40-50% measured by ALIAS.

This paper brings together twelve years of HCl measurements from six different instruments: the ALIAS *in situ* laser spectrometer on the ER-2 aircraft (1990-97), the ATMOS FTIR spectrometer on the Space Shuttle (1985-94), the MarkIV and FIRS-2 balloon spectrometers (1990-97), and the HALOE instrument on the UARS satellite (1992-96). Intercomparison of these data sets reveals an observed growth in HCl/Cl_y from 1993-97 of ~31(±9)% over five years, equivalent to 6.2(±1.8)%/year, which is ~6 times model predictions. This analysis extends that of Dessler et al., [*1997*], who identified in the HALOE data set alone a significant increase of 16(±9)% in measured HCl/Cl_y over a 3-year period (or 6.3%/year) from late 1992, which was four times larger than their model prediction, and could not be attributed to any cause. In addition, this analysis shows that the ALIAS aircraft measurements of HCl/Cly = 0.53(±0.06) in 1993 agree well with all five other direct measurements that range from 0.52 to 0.66. This range of values does not encompass the 0.86 value inferred from ClO measurements in 1993 [*Stimpfle et al.* 1994], but does agree with the lower value of 0.6±0.2 inferred from ClO measured during a 1993 balloon flight [*Avallone et al.,* 1993].

Lower stratospheric measurements of HCl

The ER-2 aircraft payload includes instruments for measuring HCl, O_3, N_2O and inorganic chlorine (Cl_y). The ALIAS instrument is a 4-channel scanning tunable diode laser spectrometer on NASA's ER-2 high-altitude aircraft. It uses high-resolution laser absorption in the 3-8 μm wavelength region [*Webster et al.,* 1994b] to directly and simultaneously measure any four of the gases HCl, NO_2, CH_4, CO, and N_2O. The instrument samples the atmosphere using a fast flow system with all interior surfaces coated with halocarbon wax. The fidelity of the measurement of HCl in the multipass cell is checked by simultaneous recording of strong CH_4 lines close to the HCl absorption line. The precision of the data varies from flight to flight, with a 1σ precision of typically ±50 to ±100 pptv. The accuracy of the measurement is about 5-7%, producing total root-sum-squared measurement uncertainties of ±10-15% for 1 ppbv. The tracer N_2O was measured directly by the ALIAS instrument, except for a few flights in which N_2O measurements from the ATLAS instrument [*Podolske and Loewenstein*, 1993] were used. O_3 was measured using UV absorption [*Proffitt et al.,* 1983].

ATMOS is a high-resolution solar occultation Fourier transform infrared (FTIR) spectrometer that has flown four times (1985, 1992, 1993, and 1994) on the Space Shuttle [*Gunson et al.,* 1996], producing vertical profiles of numerous gases. ATMOS records numerous occultations during orbit, covering a wide range of latitude.

The MarkIV spectrometer is a balloon FTIR [*Toon,* 1991] similar to ATMOS that also uses solar occultation, but with the advantage of increased integration time and true simultaneity of species measurement. The MarkIV has made ten (?) balloon flights over the period 1989 through 1997, from Ft. Sumner, NM, and Kiruna, Sweden. Species measured by ATMOS and MarkIV include N_2O, CH_4, NO, NO_2, HOCl, HCl, $ClONO_2$, CFC's, CH_3Cl, CCl_4, HCFC's, SF_6, HNO_3, CO, CO_2, H_2O, O_3, and various isotopic species.

Data from the HALogen Occultation Experiment (HALOE) [*Russell et al., 1996*] on the UARS satellite is taken directly from the published work of Dessler et al. [*1997*] and extends from July 1992 until June 1996. The HALOE instrument measures HCl,

and CH_4

The Far InfraRed Spectrometer (FIRS-2) is a Fourier-transform spectrometer that detects atmospheric thermal emission in a limb-viewing geometry [*Traub et al.,* 1991]. FIRS-2 has capability for collecting vertical profiles of several gases simultaneously, including OH, HO_2, H_2O_2 HOCl, HCl, NO_2, HNO_3, N_2O H_2O, O_3, and temperature [*Jucks et al.,* 1996].

Estimation of Cl_y and intercomparison of HCl/Cly data sets

For comparison of HCl/Cl_y values, Cl_y must first be calculated or measured. For data sets that contain a simultaneous measurement of N_2O, the relationship of Woodbridge et al. [*1995*] is used for 1992, and applied to other years with an assumed growth rate of ~2%/year for inorganic chlorine. Where N_2O measurements are not available, those of CH_4 are used to calculate Cl_y from known correlations of the two tracers [*Michelsen et al.* 1998]. The latter approach was used for HALOE and FIRS-2 data sets. Woodbridge et al. [*1995*] estimate the accuracy of Cl_y derived from the Cl_y-N_2O relationship to be about ±xx%. Dessler et al. [*1997*] estimate the accuracy of Cl_y derived from the Cl_y-CH_4 relationship to be ±20%.

For quantifying HCl/Cl_y growth rates within a single instrument data set, some systematic errors are constant throughout the time series, so that the relative accuracy may be used rather than the absolute accuracy. However, for intercomparison between measurements from different instruments, the absolute accuracy must be included with the measurement precision to describe the total uncertainty and therefore the level of agreement. For the HALOE measurements, relative uncertainty in HCl/Cl_y is ±6%, with an absolute accuracy of ±28% [*Dessler et al., 1997*]. For ALIAS, MarkIV, and ATMOS, relative uncertainty in HCl/Cl_y is typically ±5-8%, with absolute accuracies of about ±20%.

In Fig. 1, we compare measurements of HCl normalized to Cl_y that are constrained in several ways. First, all data points represent pressures ≤70 mbar, and altitudes ≤21 km. Localized ozone abundances are constrained according to $1500 \le O_3 \le 2500$ ppbv, and N_2O levels ≤260 ppbv. Furthermore, we use data points representative of mid

latitudes, and avoid including data from vortex-processed air in which HCl may be low due to earlier low-temperature PSC processing. Because the ATMOS flights of 1985, 1992, and 1993 all sampled the March/April timeframe, we have used only southern hemisphere data for these flights, and northern hemisphere data for the November 1994 flight. For the aircraft measurements, selection is done through tracer-tracer correlations [Michelsen et al., 1998]. The ALIAS data are northern hemisphere data fully constrained according to: pressure < 70 mbar, $N_2O \leq 260$ ppbv, $1500 \leq O_3 \leq 2500$ ppbv, and ClO ≤150 pptv to avoid PSC processed air. For the 1993 SPADE campaign data, flights that sampled predominantly vortex air [Michelsen et al., 1998b] are excluded. HALOE data are taken directly from the publication of Dessler et al. [*1997*], and represent the mean values of the zonally-averaged 35°N and 55°N data for each year of data. We note that the southern hemisphere data of Dessler et al. [*1997*] show similar trends.

Figure 1 shows the intercomparison of HCl/Cl_y from 1992 through 1997 for ALIAS, ATMOS, HALOE, MarkIV, and FIRS-2 data sets. In general, the data are consistent after the 1992 period of peak aerosol loading, but show significant differences during peak aerosol loading. Not shown on this plot are four data points available before the June 1991 eruption of Mt. Pinatubo (ATMOS 1985, FIRS-2, and MarkIV) which are close in value and produce a pre-eruption average of $HCl/Cl_y = 0.75 \pm$ xx. In 1992, during the peak aerosol loading, the data of Fig. 1 show widely different values for HCl/Cl_y. The FIRS-2 measurements of ~0.71 contrast markedly with the ALIAS and ATMOS measurements of ~ 0.4.

From 1993 through 1997, the data are much more consistent, and generally agree within measurement error. In 1993, all five data sets show values of HCl/Cl_y ranging from ~0.5 to ~0.7, with a mean value of 0.60 (?)± xx. These direct measurements of HCl are systematically lower than the value of 0.86 inferred from aircraft ClO measurements of 1993 [*Stimpfle et al.,* 1994], but are in excellent agreement with the balloon ClO measurements of Avallone et al. [1993] who inferred an HCl/Cl_y fraction of 0.6 ± 0.2. In November 1994, an intercomparison between the ER-2 aircraft and ATMOS measurements showed that for HCl mixing ratios of ~1 ppbv or more, the two

measurements agreed to ~10% [*Chang et al.*, 1996].

During the last year or two in which the atmosphere has recovered to aerosol levels similar to pre-eruption levels, the measurements of HCl/Cl_y in 1996/7 agree well with each other. A mean value of 0.748 ± 0.068 is measured, in excellent agreement with the pre-eruption average of 0.75 ± xx. The 1997 POLARIS mission produced the first-ever simultaneous *in situ* measurements of ClO, $ClONO_x$, and HCl. The *in situ* and remote sensing measurements made at the same time show a remarkable consistency between all three measurements and an ability to close the inorganic chlorine budget to better than 90% [*Bonne et al.*, 1998; *Sen et al.*, 1998].

Conclusions

This paper brings together HCl measurements from six different instruments: the ALIAS *in situ* laser spectrometer on the ER-2 aircraft (1990-97), the ATMOS FTIR spectrometer on the Space Shuttle (1985-94), the MarkIV and FIRS-2 balloon spectrometers (1990-97), and the HALOE instrument on the UARS satellite (1992-96). Intercomparison of these data sets reveals an observed growth in HCl/Cl_y from 1993 through 1997 of ~31(±9)% over five years, equivalent to 6.2(±1.8)%/year, which is ~6 times model predictions. This growth rate agrees well with that observed in the HALOE data alone by Dessler et al., [*1997*], namely, an increase of 16(± 9)% in measured HCl/Cl_y over a 3-year period (or 6.3%/year) from late 1992, which was 4 times larger than their model prediction.

Our analysis shows that the ALIAS aircraft measurements of HCl/Cly = 0.53 in 1993 agree well with all five other direct measurements that range from 0.52 to 0.66. This range of values does not encompass the 0.86 value inferred from ClO measurements in 1993 [*Stimpfle et al*. 1994], but does agree with the value of 0.6±0.2 inferred from ClO in a 1993 balloon flight [*Avallone et al.*, 1993].

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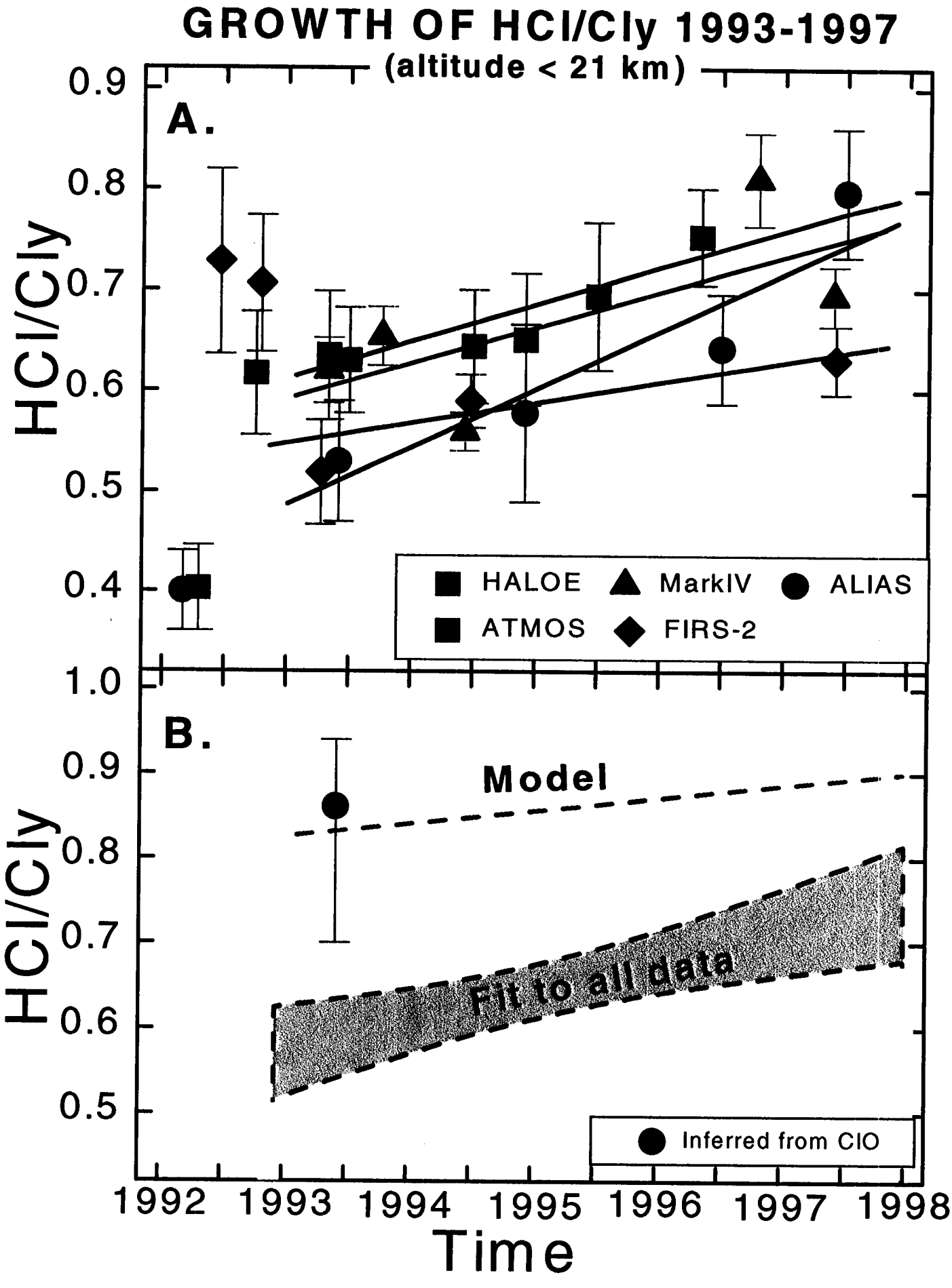
Figure 1.

A. Satellite, Space Shuttle, aircraft, and balloon measurements of HCl/Cl_y below about 21 km. Data points are constrained as described in the text. Lines are linear fits to individual data sets (except that of ATMOS) from Jan 1993 through December 1998. B. Linear fit to all data with shaded region representing 96% (2 sigma) confidence limits, for comparison with model calculation (red dashed line) and mean HCl/Cl_y value inferred from aircraft measurements of ClO [*Stimpfle et al.,* 1994].


GROWTH OF HCl/Cly 1993-1997
(altitude < 21 km)
A.
B.
HCl/Cly
0.9
0.8
0.7
0.6
0.5
0.4
1.0
HALOE
MarkIV
ALIAS
ATMOS
FIRS-2
Model
Fit to all data
Inferred from ClO
1992
1993
1994
1995
1996
1997
1998
Time